VII. Infrared Spectroscopic Methods

I. Purpose

a. To become familiar with the principles of IR spectroscopy, and then to use them to identify and measure gaseous organic solvents in a mixture.

b. To review the concept of exponential decay and to measure the air exchange rate under varied conditions using an infrared continuous monitoring instrument.

c. To learn the use of an exponential dilution chamber for the calibration of direct reading instruments.

II. Readings

McDermott	Infra-red	Ch. 12
Kenkel (ACT)	Theory of operation	pg. 220-233
ASI	MIRAN	pg. 511-512 & 531-534

III. Outline

Part 1: Measurement of room ventilation rates. (Period 1)

Part 2: Analysis of gaseous organic solvents. (Period 2)

Part 3: IR calibration using a dilution chamber. (Period 1 or 2)

You should do Parts 1 and 2 in the order shown. You will probably have enough time to do all three parts, but if not, the third part can become optional if requested.

The instrument manual for the MIRAN 1-A is available in the laboratory and in F226. Pay special attention to sections 3.2, 3.3, and 3.4 covering spectra scanning, cell calibration, and sampling and operating procedures. The reading assignment in McDermott covers important concepts such as calibration procedures, closed sample loop systems, and typical solvent wavelength and pathlength settings for IR measurements.

Definition of IR terms.

Pathlength: This is the distance the IR beam must travel through the gas sample, between the light source and the detector. This is most important when using the gas cell on the analyzer because the pathlength influences the instrument's sensitivity. The longer the pathlength, the farther the beam must travel through the sample before it reaches the detector, and the greater the probability the beam will encounter the molecules of interest. A longer pathlength therefore provides greater sensitivity and is desirable for analyzing lower gas concentrations; higher concentrations will absorb more of the light and consequently a shorter pathlength is needed.

The pathlength is adjustable between 0.75 and roughly 21 meters, but must be set at certain increments (i.e. 0.75 m, 2.25, m, 3.75 m, and so on) - the range is not continuous. Pathlength is controlled by turning the dial on the end of the gas cell. The dial adjusts mirrors inside the cell which rotate into and out of the beam's path depending on the pathlength desired. The pathlength is optimized by adjusting the dial slightly above and below the pathlengths corresponding numerical setting until it is at the point where the mirrors are optimally aligned (i.e. focusing the most and scattering the least amount of light). When in the absorbance mode, the optimum corresponds to the minimum absorbance; in the transmittance mode it corresponds to the maximum transmittance.

Wavelength: The analytical wavelength is chosen for quantitative analysis of a material. Since light absorption is dependent upon the number and types of bonds present on a molecule, a compound may have several wavelengths that absorb strongly. It is important to select a wavelength that will give the best resolution (the greatest absorbance compared to background) and, if analyzing a mixture, a wavelength that is not absorbed by any of the other compounds.

Transmittance (T): This is the ratio of light energy passing through a sample and reaching the detector to the amount of incident light. Transmittance is usually reported as %, and is most useful for scanning to determine a compound's characteristic wavelengths for maximum absorption. Transmittance is generally plotted on a log scale, permitting resolution that would require a huge linear scale for qualitative scans.

Absorbance (A): This is the logarithm (base 10) of the reciprocal of the transmittance:

$$A = \log_{10}\left(\frac{100}{\%T}\right)$$

Absorbance, unlike Transmittance, is linearly related to concentration of a material (A = abc, where a is the absorption coefficient, b is the path length, and c is the concentration of absorbing gas). Absorbance is generally used for quantitative analysis.

Scanning: Scanning is a way of asking, "What types of molecular bonds are present?" (i.e. where does absorbance occur; therefore, what compounds might be present?) The ability of a compound (or mixture) to absorb light over a range of wavelengths reveals its identity. Scanning is generally used for qualitative analysis, and is normally conducted in the Transmittance mode. The scan proceeds automatically at a constant rate by turning the spectral filter with an internal motor. When connected to a chart recorder the scan provides a graphic representation of characteristic absorptions (called the absorption spectrum) and this can be used to identify compounds or to determine a suitable wavelength for quantitative analysis.

Slit width: This selector controls the amount of light passing through the sample to the detector. For normal operation, the 1mm slit width is generally used.

Gain (older model) or Fine zero control (newer model): This varies the detector signal amplification. It is used for adjusting the Absorbance and Transmittance ranges for the meter.

High-Low (old) or Coarse zero control (new): This switch affects the gain or fine zero control. In the low position the control is amplified by a factor of one, and in the high position by a factor of ten. The high position is required for most applications.

Open cell system: Air enters the cell directly from the room or sample location and leaves the cell via the built-in sample pump into either the room or a laboratory hood.

Closed cell or Closed loop system: Air is recirculated from the cell, to the external circulating pump and back to the cell. The output of the pump is attached to the inlet of the IR cell.

WDIR vs. FTIR: Most laboratory based Infrared spectrophotometers have greater resolution and sensitivity for the identification and quantification of gases and vapors than does the MIRAN. Two different types of laboratory instruments can be used for this purpose: wavelength dispersive infrared (WDIR) and Fourier Transform infrared (FTIR.) Example spectra are provided from each type in the Appendix.

Part 1: Room Ventilation Measurement Using Tracer Gas Decay

Equipment

a. MIRAN 1A -IR spec.
b. re-circulating pump
c. liquid syringes
d. stopwatch
e. assorted tubing
f. gas syringes
g. large blower or fan
h. chart recorder

In this part, you will use the MIRAN to measure the ventilation rate of **two laboratories and one office**. You will do this by dispersing an inert tracer gas in the room and then using the MIRAN 1A to measure the tracer concentration decay over time.

Background

After a tracer material is released and dispersed in a room, its concentration will decay as tracer-free air is brought in by the ventilation system and, possibly, as other removal processes occur. The equation which approximates this decay, assuming a well mixed room, is

$C = C_0 e^{-kt}$, where

$k = \frac{\text{ventilation rate into room}}{\text{room volume}}$, k has dimensions of $m^3/(t \times m^3) = 1/t$

C_0 = initial tracer concentration C = tracer concentration at any time, t

e = base of natural logarithms

The coefficient k is equivalent to effective air exchange rate. When plotted on linear graph paper the room decay readings will be in the form of an exponential decay curve.
If the decay equation is presented in logarithmic form it becomes: $\ln C = \ln C_0 - kt$. Because concentration C is proportional to Absorbance (but not to %T), A can be substituted for C and plotted.

Thus plotting the decay equation on semi-logarithmic graph paper should give a straight line with a slope of -k. The slope of the line (and the resulting k) is properly computed as:

$$\text{slope} = -k = \frac{\ln C_2 - \ln C_1}{t_2 - t_1} = \frac{\log C_2 - \log C_1}{t_2 - t_1} \times 2.303 = \frac{\ln A_2 - \ln A_1}{t_2 - t_1}$$

where C_1, C_2 (or A_1 and A_2) are readings at times t_1 and t_2. Estimate the air exchange rate for each room.

Pre Class Preparation

1. Read over the MIRAN instrument manual. Pay special attention to sections 3.2, 3.3 and 3.4 covering spectra scanning, cell calibration, sampling and operating procedures.

2. Review the IR spectral scan for the tracer (provided by the instructors). Note the wavelengths with peak absorbance in wave numbers (cm^{-1}) and micrometers.

Procedure

1. Set up a closed cell system (MIRAN 1A, circulating pump), set the MIRAN in the Transmittance mode and attach the chart recorder to the MIRAN. Run two scans of room air in the cell from 8 to 14 micrometers. Inject 100 μL of tracer gas into the closed cell system. Take two or more spectral scans (8-14 μm) to determine first the optimum wavelength and then the optimum pathlength for the tracer peak. Optimum means the greatest deflection. For this experiment we will assume that absorbance varies linearly with tracer concentration, so no calibration will be necessary.

2. With the optimum wavelength and pathlength set, empty the cell and re-zero. In absorbance mode and with a closed gas cell system, add tracer to the IR cell until the meter reads full scale. Calculate the concentration of tracer in the MIRAN chamber. Set up the system for open system (rearrange the connection at the outlet of the pump), turn on the chart recorder movement, and observe the concentration decay rate. This will be representative of the fastest decay rate that the system can measure. Any room decay rate slower than this can be measured.

3. Move to the room that you wish to measure. Set up an open gas cell system with room air being drawn through the MIRAN. Set the MIRAN using the absorbance mode for the previously determined wavelength and pathlength for tracer (as in 1.). Release tracer gas into the room. You may wish to use a large blower or fan to disperse the tracer. When the MIRAN response is driven full scale, stop releasing tracer and turn on the chart recorder. Using the stopwatch or marking the recorder tracing, record the MIRAN absorbance response and the elapsed time at regular intervals as the tracer gas decays.

4. Repeat this procedure under various conditions (doors open, closed; hood open, closed; fan on, off; in different locations, etc.) and in different rooms. Be sure to measure room F226.

5. In your write-up prepare graphs of ln (C) or ln (A) versus time and determine the air exchange rate (k in units of room changes per hour) for each of the rooms/conditions which you measured. Discuss the factors that would affect the precision and accuracy of this method.

6. Discuss the air quality of the office area. Combine the direct reading data logged with the IR room decay data to draw a conclusion.

Part 2: Analysis of Gaseous Organic Solvents

Equipment

a. MIRAN 1-A IR spec.
b. Recirculating Pump
c. liquid syringes
d. Strip-chart recorder
e. assorted tubing

In this part you will use the IR spectra to qualitatively identify the organic contaminants in a sample atmosphere prepared by a dynamic gas generating system. The generator system will simulate the solvent exposures in a hypothetical workplace. You will then calibrate the MIRAN for the identified solvents and quantitatively determine the exposure at the output of the generating system. Use FTIR/WDIR data in the appendix to assist in identification.

Pre Class Preparation

1. Review the spectral scans in the Appendix to identify the possible solvents (the unknown has three components). Determine what spectral wavelengths will be optimal for quantitatively measuring each organic solvent. Pay attention to possible spectral interferences of the compounds that are present in the same environment.

2. You will inject measured volumes of liquid solvents into the MIRAN to calibrate the instrument. The volume of the MIRAN cell chamber and assorted tubing is 5.6 L. **Prior** to the lab period make up a chart showing the amount of the organic solvent liquid (in uL) to be injected into the MIRAN gas cell chamber to create a vapor standard concentration at the TLV.

(μl liquid = TLV in mg/m^3 x volume air (m^3)/ ρ_L(mg/μl)),
where ρ_L is the liquid solvent density.

In Class Experiment

1. A FTIR scan of the unknown mixture is included in the Appendix. Compare this IR scan with the IR scans of pure compounds in the appendix to the lab manual. Determine which three of the eight possible compounds are present. Some of these scans will include FTIR and/or WDIR spectra.

2. Assemble the MIRAN equipment in a closed cell configuration. Have an instructor check your set-up. Run one background scan from 2.5 to 14 micrometers with room air in the cell. This will show the wavelengths where water and carbon dioxide absorb and where filter changes occur. Inject approx. 5 μL of the liquid solvent mix, or generator effluent provided by the instructor. Make a scan or scans at one or more pathlengths, to confirm your prior qualitative determination, to determine the exact wavelength setting of the characteristic peak for each solvent on this instrument, and to determine a suitable pathlength for each solvent. When completed, open the gas cell system, with room air entering the MIRAN chamber and exhausting cell air through the vacuum line or into a laboratory hood. Flush the chamber for at least two minutes.

3. Calibrate the MIRAN for each of the three solvents using the absorbance mode. Calculate the liquid volume required for 0.25, 0.5, 1.0 and 5.0 times the TLV concentration for each of the identified solvents. Set the pathlength for the optimum value that you have determined for the first solvent (The chart on the lab door is a guide). Empty the cell, then record the wavelength, pathlength and zero setting. Set up the closed cell system and inject the liquid volume corresponding to the least concentrated standard. Record absorbances! You may manually adjust the wavelength to the characteristic peak for that solvent and obtain your measurement from the Wilks-MIRAN meter; or you may scan a small part of the spectrum that includes the peak and obtain your measurement on the chart recorder, or you may do both. Empty cell and inject the liquid volumes that will create a concentration equal to the next level. Repeat this process until you have run each of the standard concentrations for this solvent. Hint!! The highest standard concentration should be nearly full scale (>0.74) absorbance. When completed, flush out the system and repeat the process for each of the other solvents. Graph the peak responses for the absorbance of each solvent to verify linearity.

4. Sampling of the unknown mixture: adjust the tubing so that the MIRAN outlet is connected to the vented exhaust line and the inlet is connected to the dynamic gas generating system. Allow the sample atmosphere to flow through the MIRAN for 2 - 3 minutes to purge the cell. Using the settings obtained in step 3 above (wavelength, pathlength, and zero), determine the absorbances and the concentration for each solvent.

Report

1. Show your qualitative identification by peak locations in the spectra of the unknown mixture.
2. In your write-up show a table of calculations for the calibration curve for each solvent, and then graph the calibration curves. Determine the concentrations present in the sample atmosphere. Discuss the factors that would affect the accuracy of your results and the precision of your measurements.

3. Discuss potential hazard posed by airborne exposures to these solvents.

Part 3: IR Calibration Using a Dilution Chamber

The procedure provides a time saving method for preparing a multi-point calibration curve for direct reading instruments. In this part you will calibrate the MIRAN by injecting a known amount of a compound into the MIRAN (or into a chamber of known volume in series with the MIRAN) and then recording the MIRAN response over time as the concentration decays exponentially. This is analogous to room ventilation rate measurements, except that because you know the beginning concentration and the system volume, you can calculate the concentration at numerous set times thereafter. You can use these calculated values to calibrate the MIRAN over a wide dynamic range. This wide range should allow you to determine the linearity (or lack thereof) of the instrument's response and to obtain a MIRAN calibration curve in a minimum time.

Background

You may assume instantaneous dilution (complete mixing as long as the air is stirred) in the calibration chamber. Using this assumption, the concentration at any time after the dilution commences, will vary, as follows:

$$C_t = C_i e^{-Qt/v}$$

where C_i = initial concentration, PPM

C_t = concentration at time t, PPM

V = MIRAN volume, 5.6 liters

Q = flow rate, L/min

t = time elapsed, min

This equation applies to dilution with clean air only.
Another form of the dilution equation that simplifies the graphical presentation is:

$$C_t = C_i e^{-t/r} \quad \text{where } r = V/Q$$

In this form, a plot of ln C against t will yield a plot having a slope of -1/r, where r is the time (min) for 1 system air exchange.

Using conventional coordinates, the concentration against time plot will show exponential decay. Conversely, a semi-log (ln C v. time) plot will give a straight line.

To calibrate instrumental response as a function of concentration, a series of readings are made over a specified time period. These observed readings are plotted and compared to the calculated readings to determine linearity of response. The recorder will give an Absorbance vs. time graph. Combined these data give C vs. A plot.

Several graphical presentations should be made of your data. Plot instrumental readings against time on linear and on semi log-paper. For the dilution run, the results should show exponential decay on linear paper and should form a straight line on semi-log paper. Indicate the calculated concentrations on the same graphs. To obtain a calibration curve for the instrument, make a separate plot of the instrument reading on the ordinate (y axis) against the corresponding calculated concentration on the abscissa (x axis).

Two or more repetitions of the calibration should be made to determine the errors associated with this procedure.

Alternatively, this procedure could be used in reverse, by starting with a concentration of zero ppm tracer and supplying a known concentration of tracer at a known total flow rate of 2-5 L/min. The relevant equation is:

$$C_t = C_{max} - C_{max}e^{-t/r} = C_{max} - C_{max}e^{-Qt/V}$$

Where, C_{max} is now the asymptotic maximum concentration approached as t increases. This is the growth form of the previous equation.

Procedure

1. Assemble the equipment as shown in Fig. 1 below.

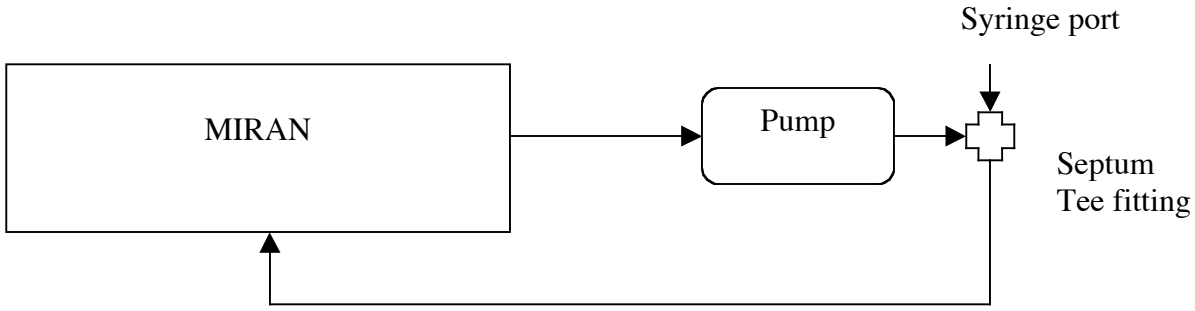
2. Inject a measured volume of the compound for which you wish to calibrate the MIRAN. You may use tracer gas, or any of the calibrated liquid solvents. Allow time for the compound to disperse uniformly in the system (to maximum constant reading and concentration).

3. Open the MIRAN inlet connection as shown in Fig. 2 to dilute the concentration with a constant flow rate of room air as measured with the rotameter. Record the MIRAN response over time as you did in the room ventilation measurements. Using a strip chart recorder is advantageous. You may repeat the procedure for the other compounds.

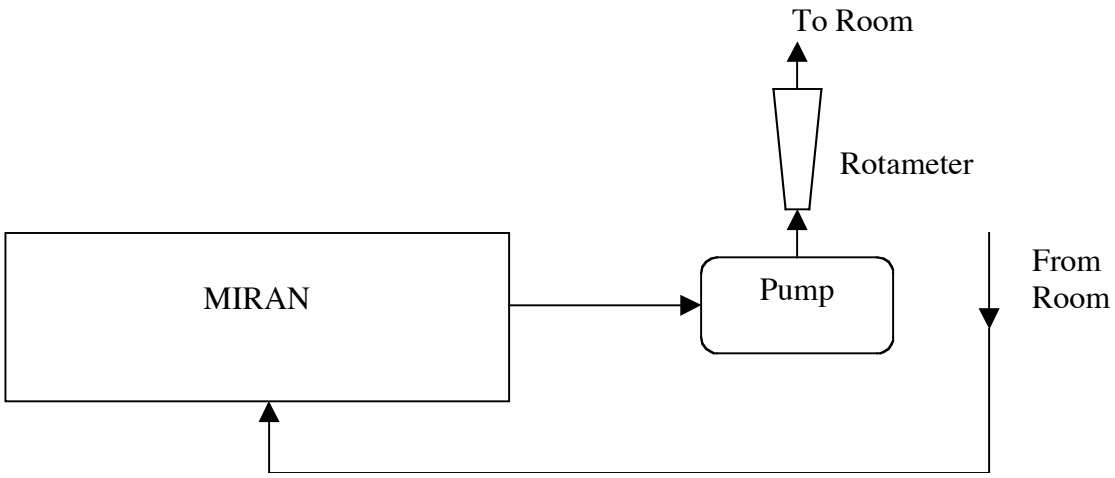
4. In your report prepare response curves for each compound. Is there a linear range? Comment on the factors that would affect the accuracy and precision of this method.

Schematic Diagram of an Example of the Dilution Chamber Calibration Apparatus:

1. injection of tracer and mixing within the system



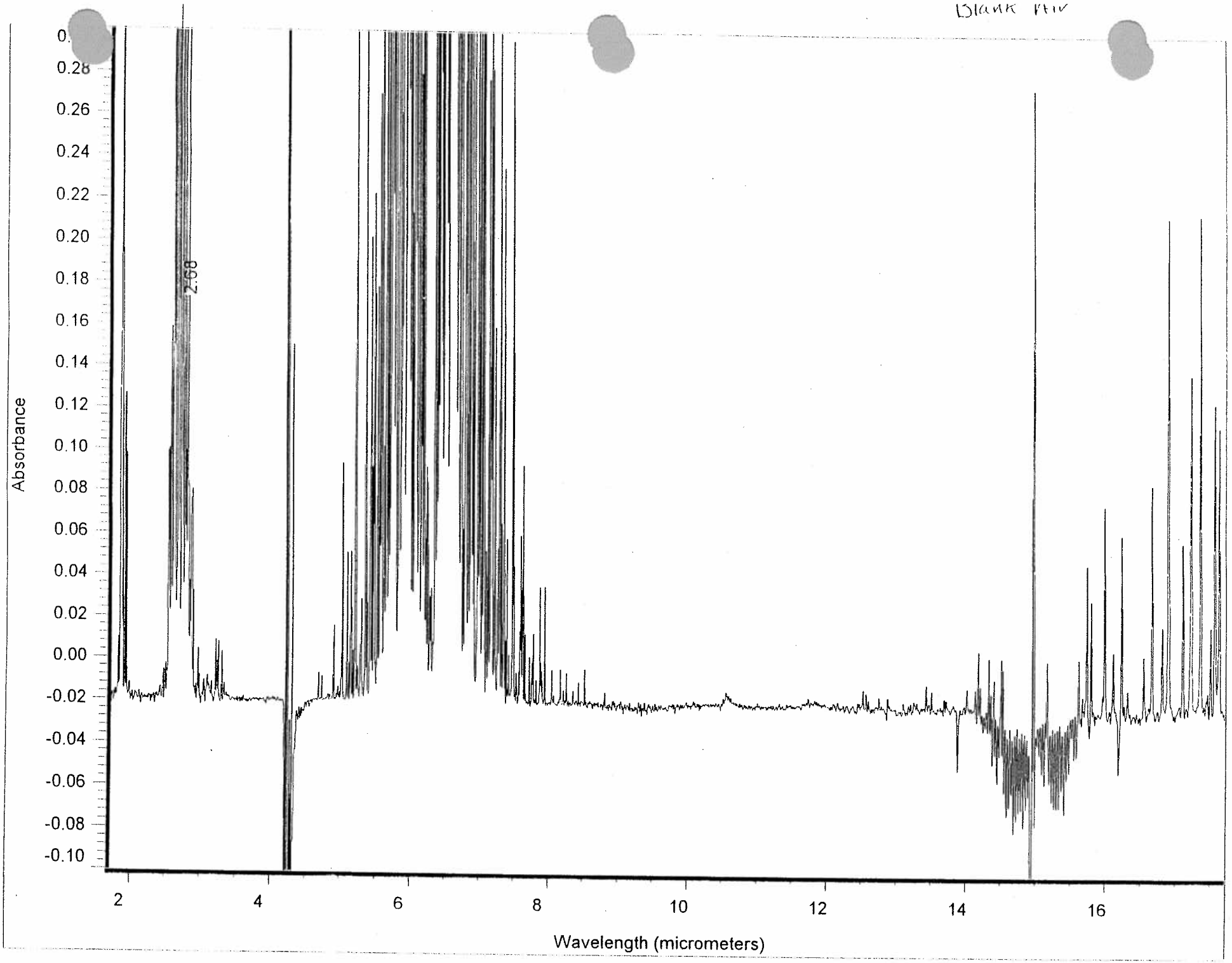
2. dilution of tracer at a known rate

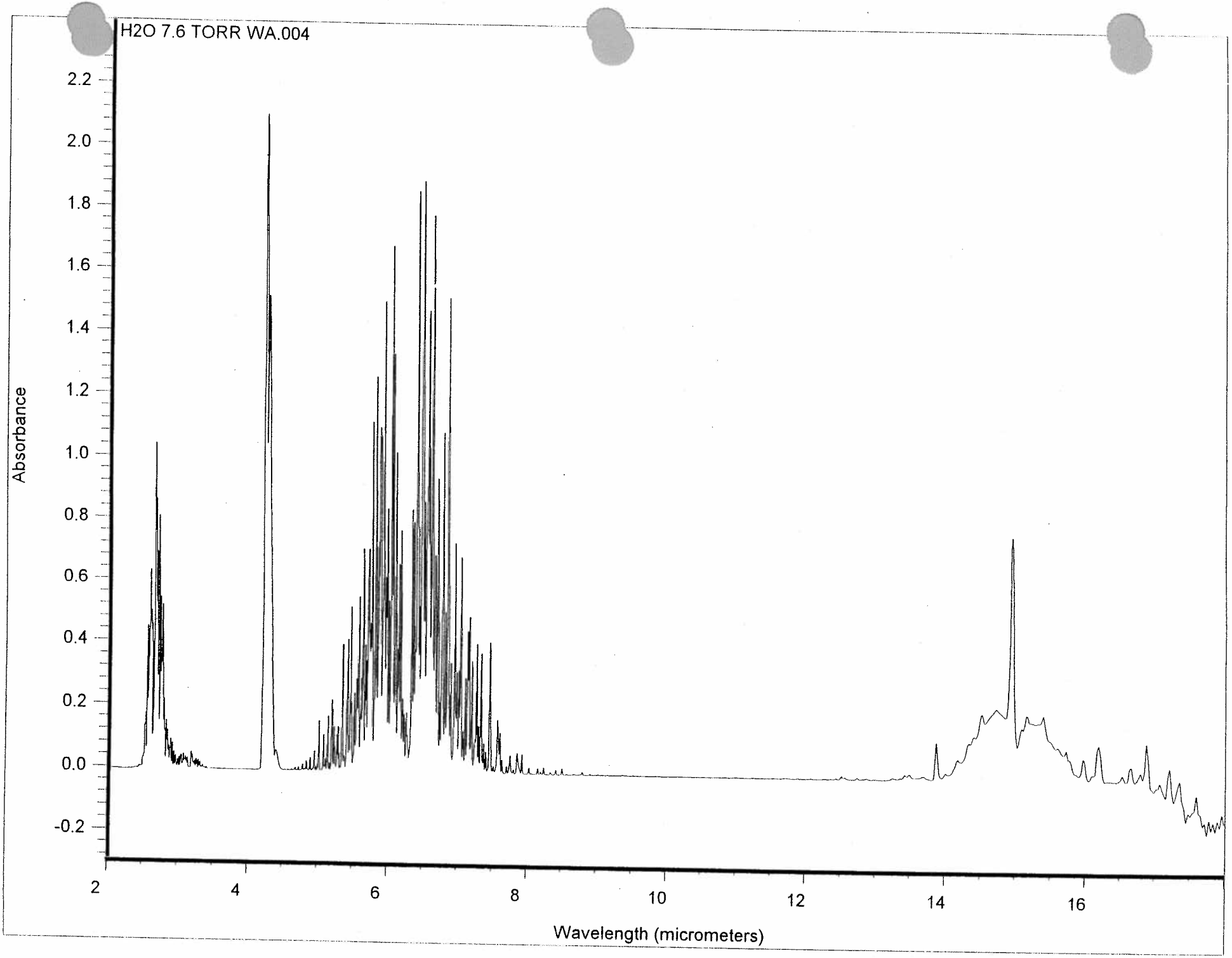


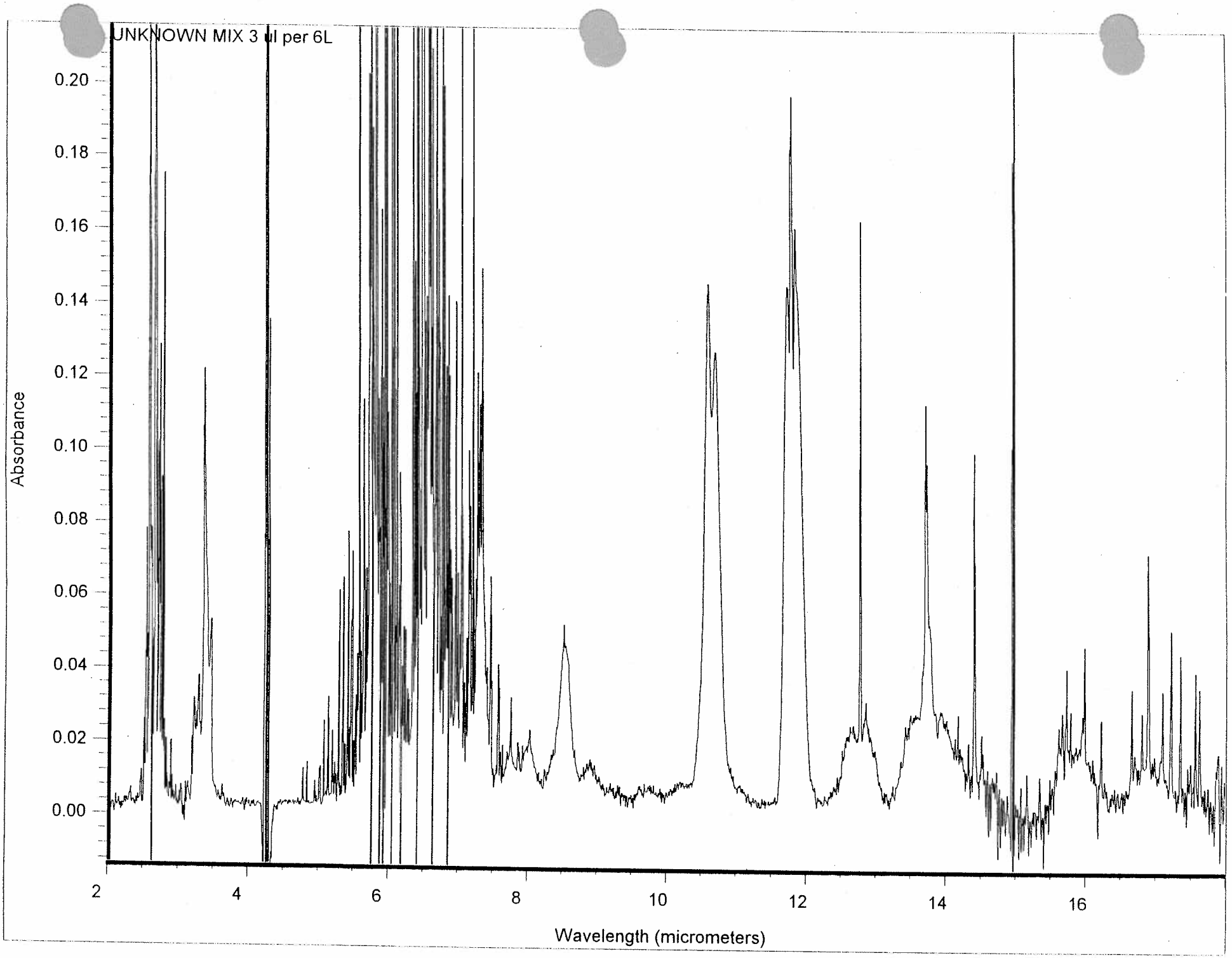
Infrared Spectroscopic Methods

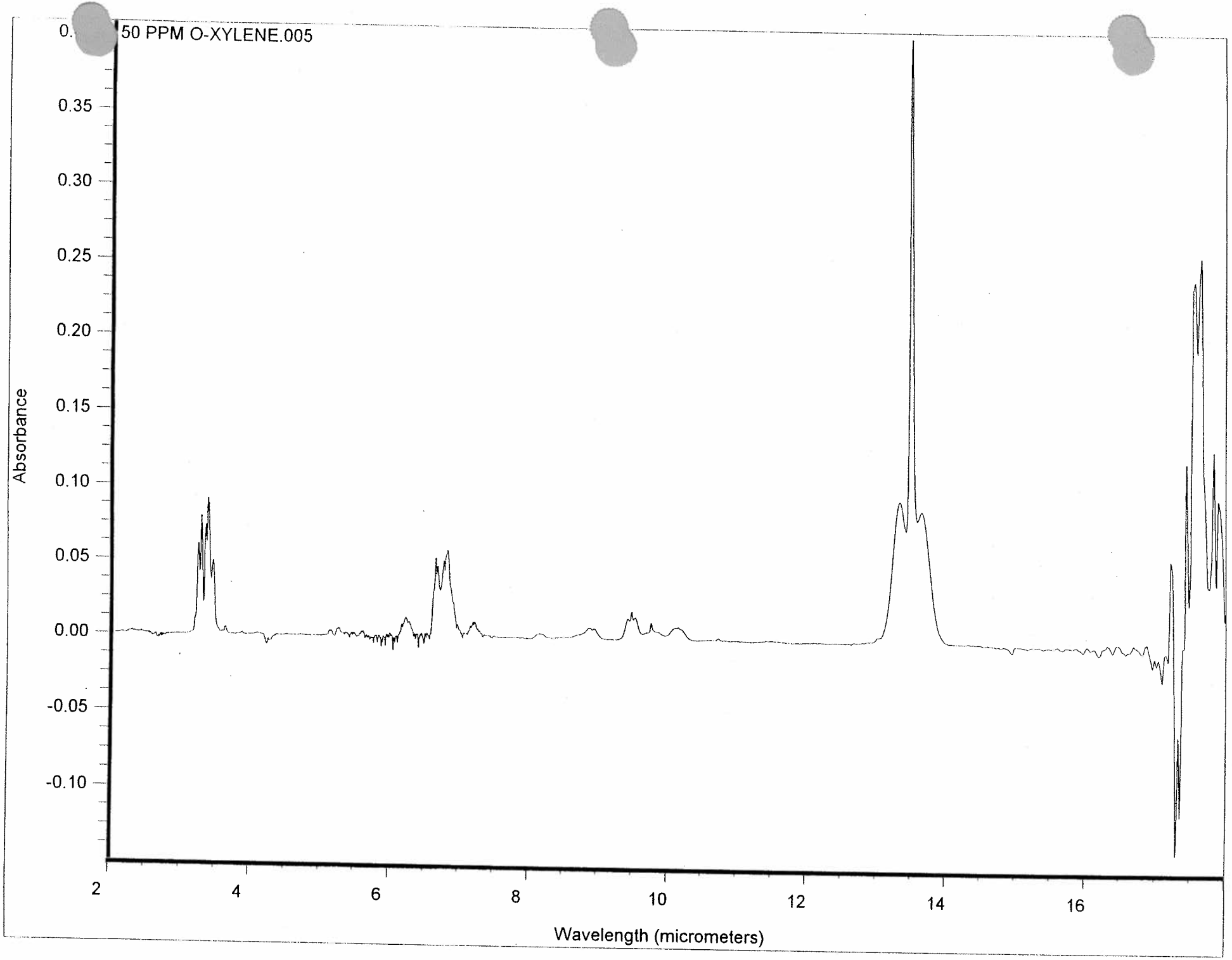
APPENDIX – IR Spectra of Individual Compounds and Mixtures

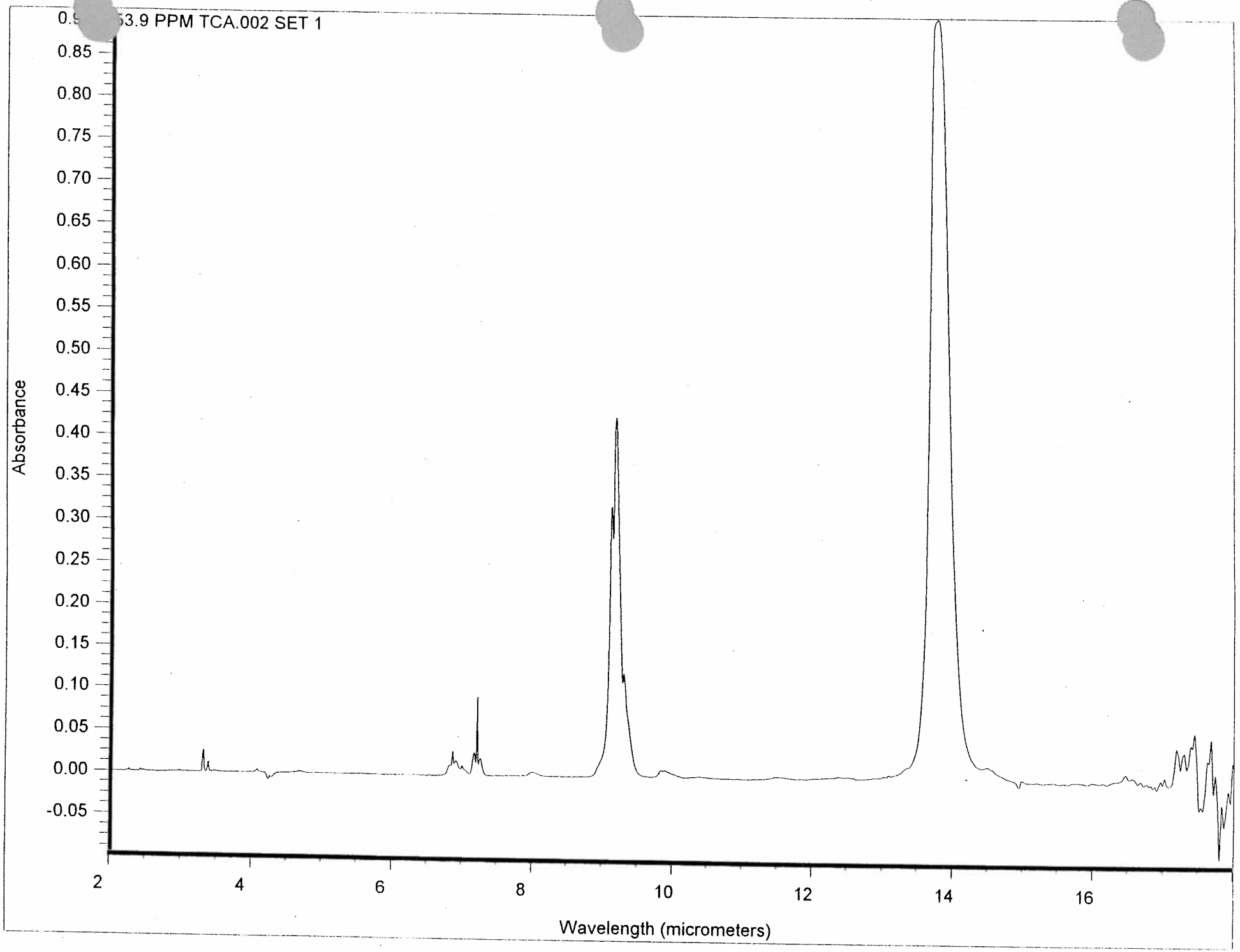
1. Blank (clean) air
2. Water vapor in air
3. Unknown mixture
4. o-Xylene
5. 1,1,1-trichloroethane
6. Acetone
7. Ethyl acetate and Methyl ethyl ketone
8. Trichloroethylene
9. Trichloroethylene and Toluene
10. o-Xylene and m-Xylene

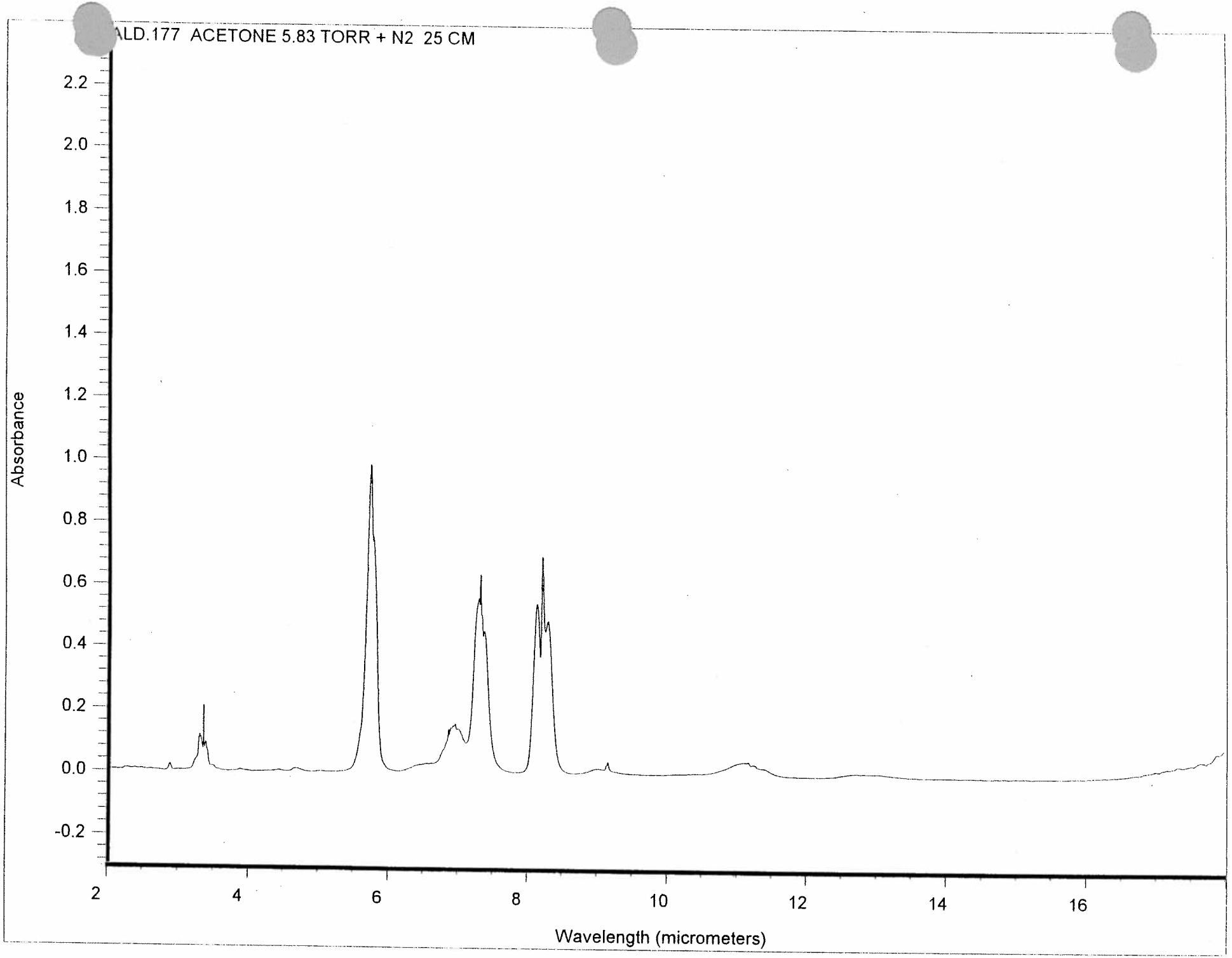

Blank RAV
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
Absorbance
2.68
2
4
6
8
10
12
14
16
Wavelength (micrometers)

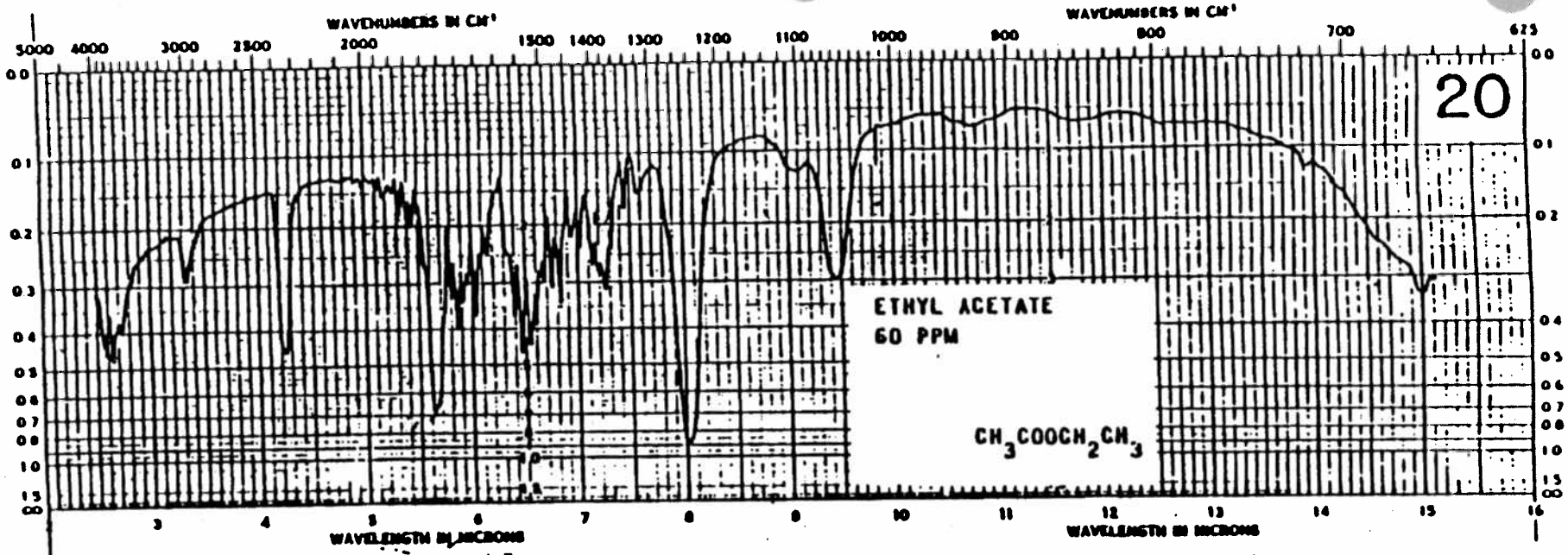

H2O 7.6 TORR WA.004
Absorbance
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
2
4
6
8
10
12
14
16
Wavelength (micrometers)

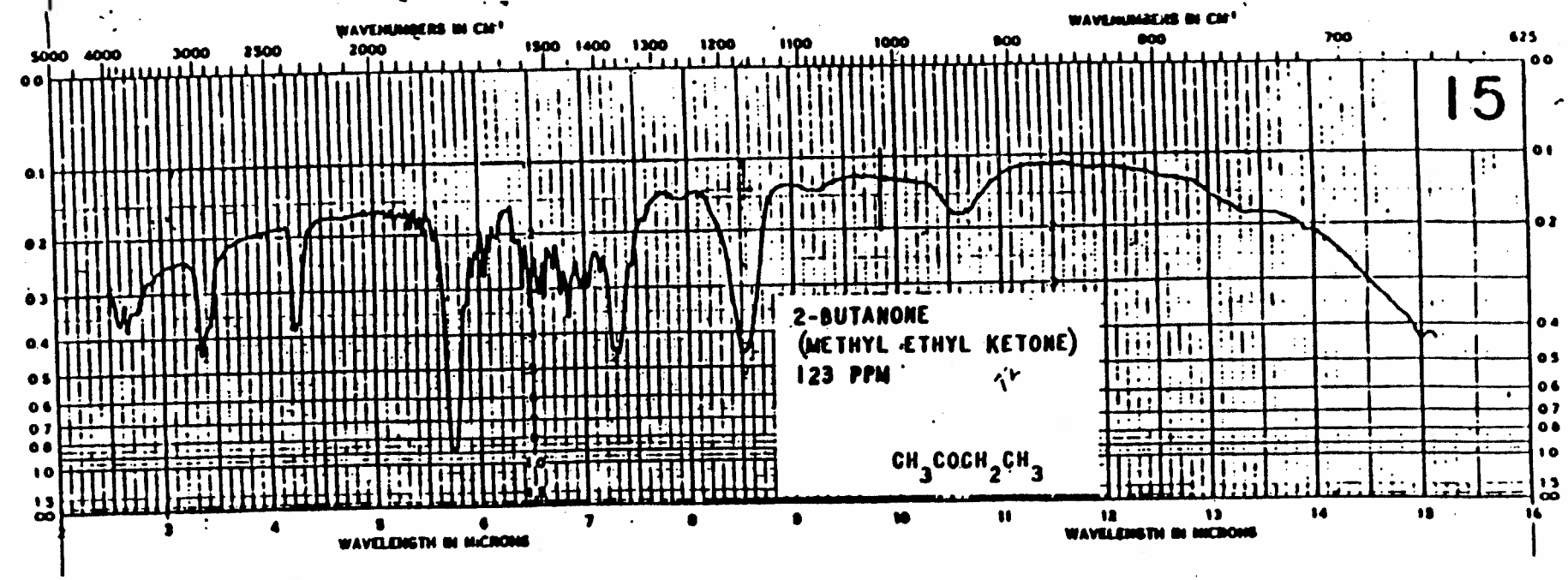

UNKNOWN MIX 3 ul per 6L
Absorbance
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
2
4
6
8
10
12
14
16
Wavelength (micrometers)

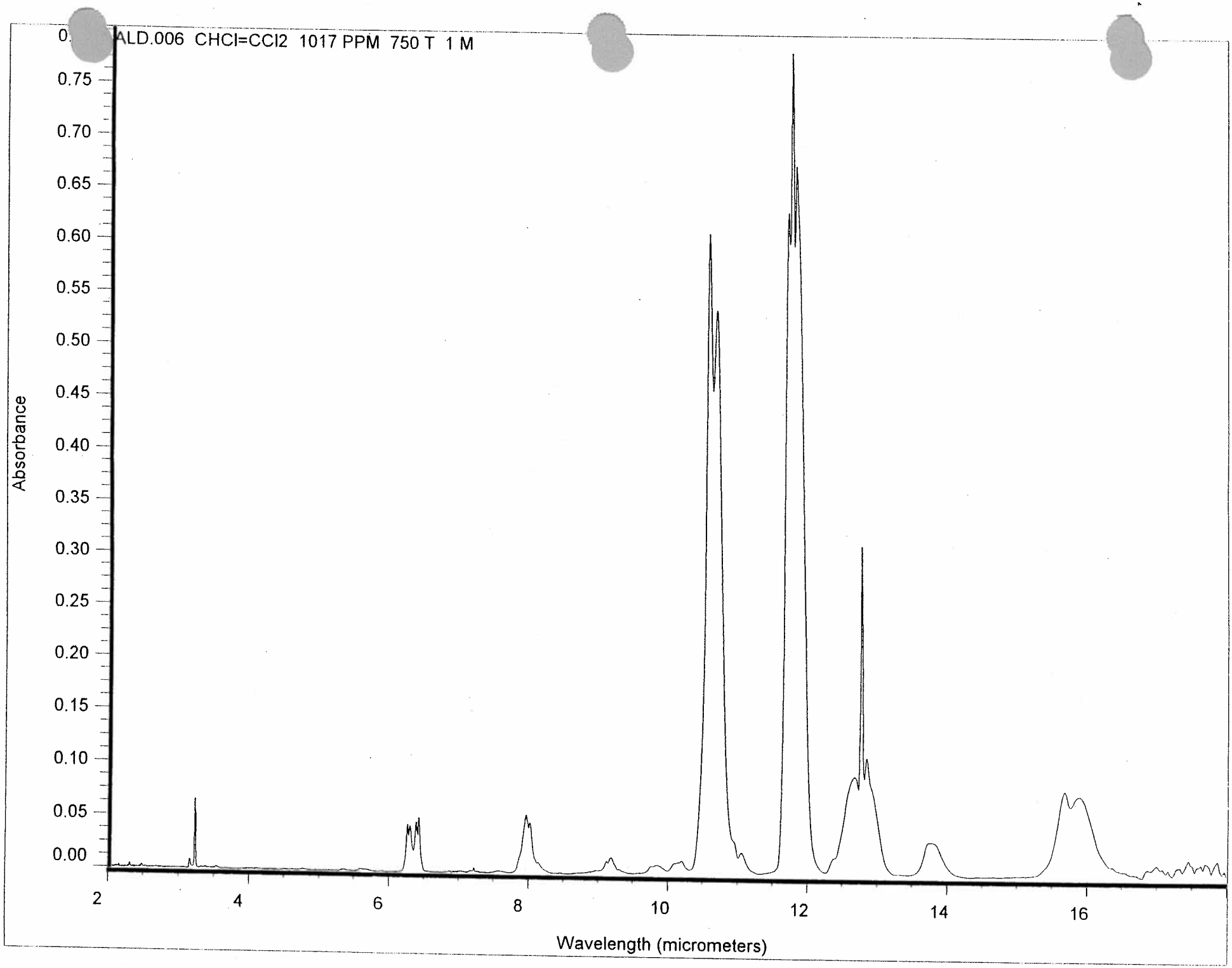

50 PPM O-XYLENE.005
0.
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
Absorbance
2
4
6
8
10
12
14
16
Wavelength (micrometers)

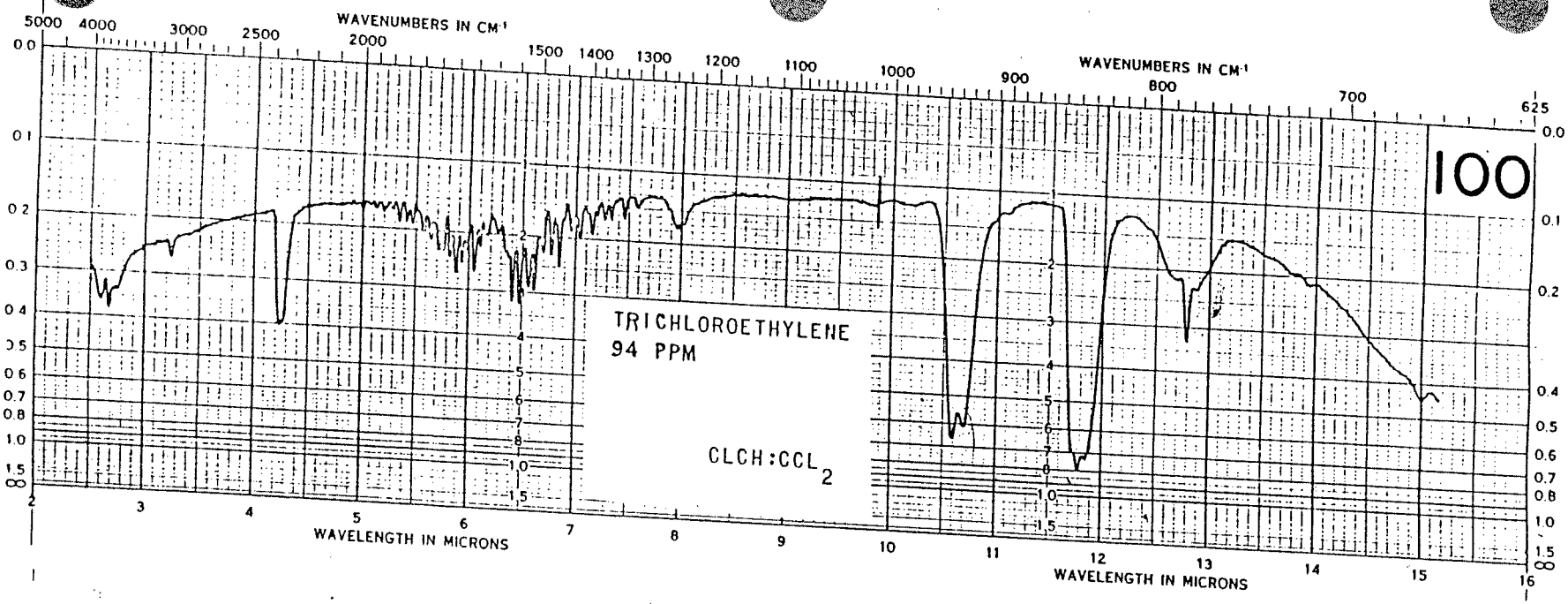

53.9 PPM TCA.002 SET 1
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
Absorbance
2
4
6
8
10
12
14
16
Wavelength (micrometers)

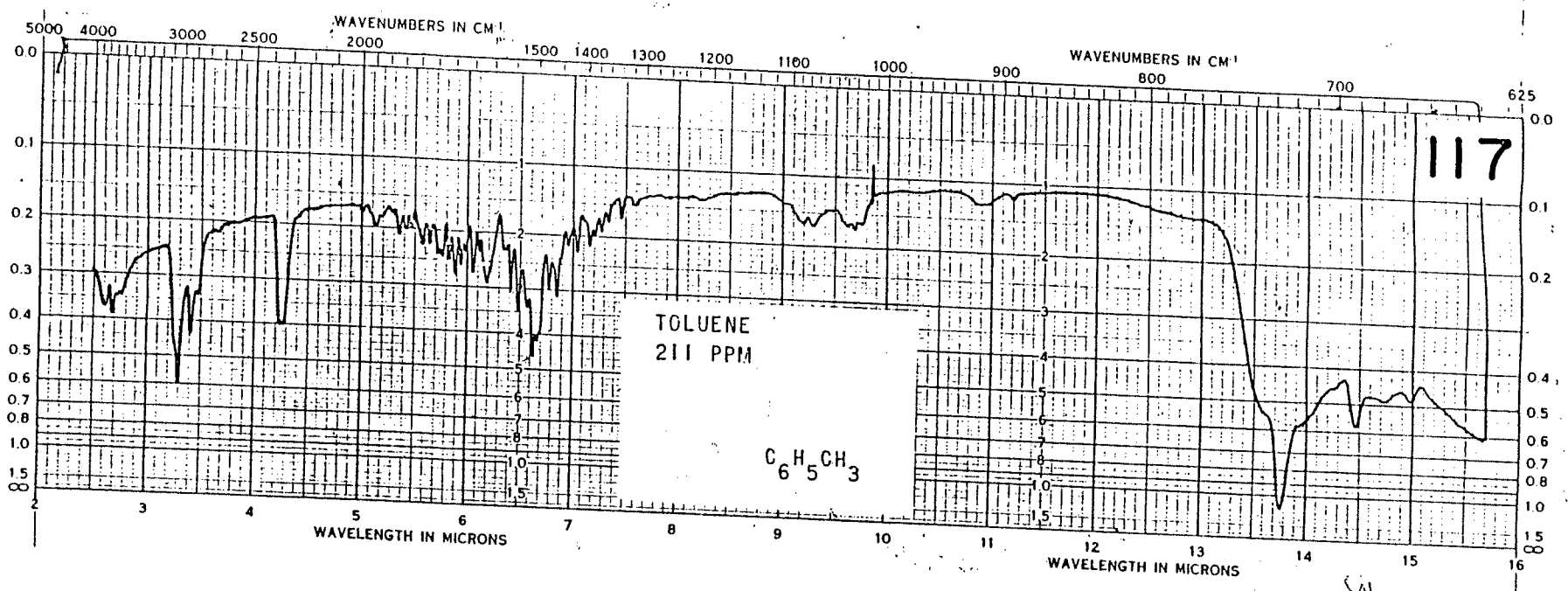

ALD.177 ACETONE 5.83 TORR + N2 25 CM
Absorbance
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
2
4
6
8
10
12
14
16
Wavelength (micrometers)

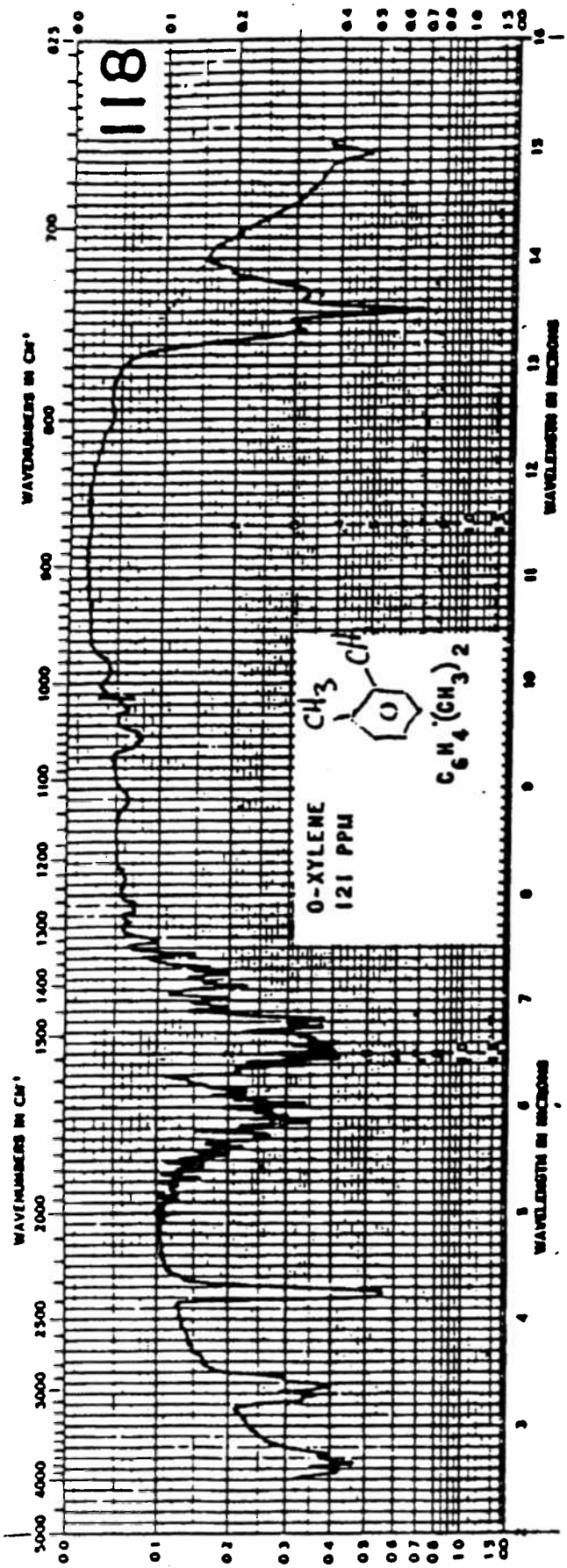

WAVENUMBERS IN CM⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVELENGTH IN MICRONS
3 4 5 6 7 8 9 10 11 12 13 14 15 16
20
ETHYL ACETATE
60 PPM
CH3COOCH2CH3

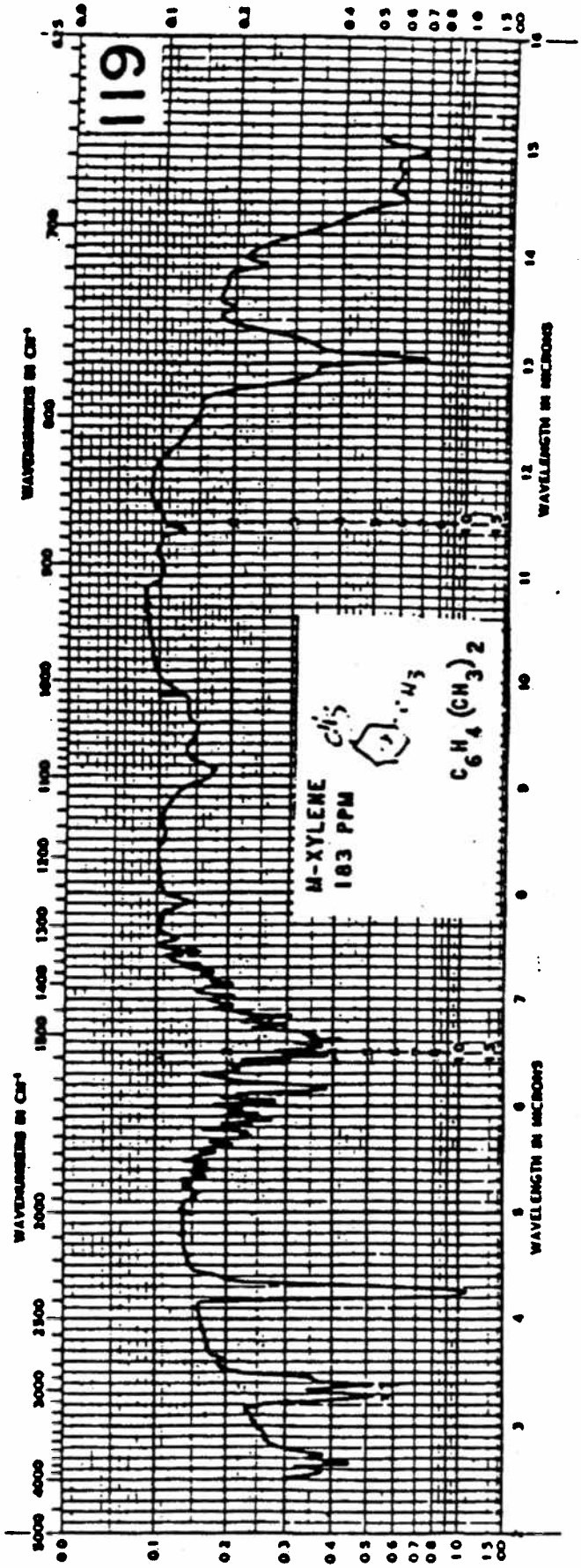

WAVENUMBERS IN CM⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVELENGTH IN MICRONS
3 4 5 6 7 8 9 10 11 12 13 14 15 16
15
2-BUTANONE
(METHYL ETHYL KETONE)
123 PPM
CH3COCH2CH3

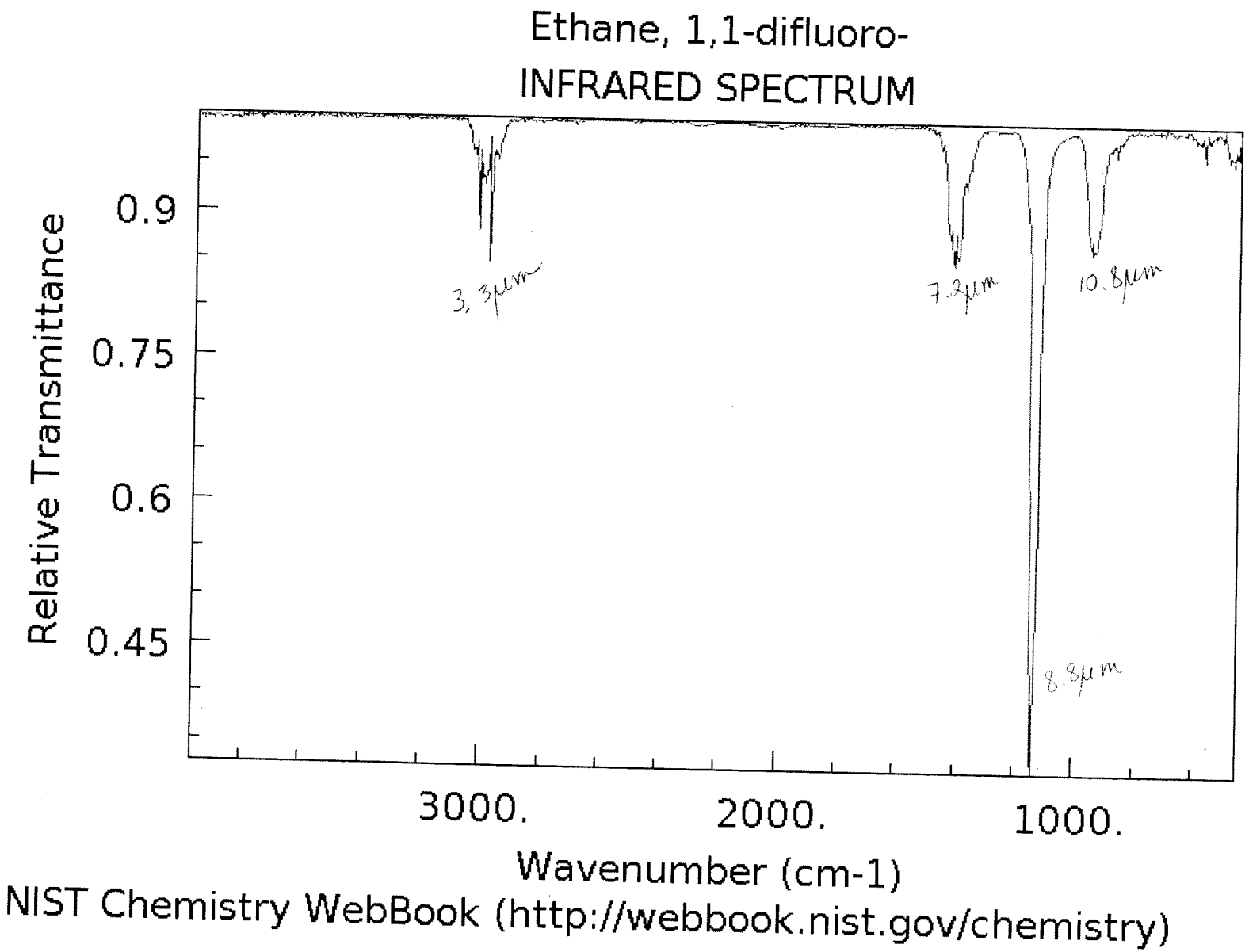

ALD.006 CHCl=CCl2 1017 PPM 750 T 1 M
Absorbance
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
2
4
6
8
10
12
14
16
Wavelength (micrometers)


WAVENUMBERS IN CM⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVELENGTH IN MICRONS
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
TRICHLOROETHYLENE
94 PPM
CLCH:CCL2
100


WAVENUMBERS IN CM⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVELENGTH IN MICRONS
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
TOLUENE
211 PPM
C6H5CH3
117


118
O-XYLENE
121 PPM
$C_6H_4(CH_3)_2$
WAVENUMBERS IN CM⁻¹
WAVELENGTH IN MICRONS


119
M-XYLENE
183 PPM
$C_6H_4(CH_3)_2$
WAVENUMBERS IN CM⁻¹
WAVELENGTH IN MICRONS


Ethane, 1,1-difluoro-
INFRARED SPECTRUM
Relative Transmittance
0.9
0.75
0.6
0.45
3.3μm
7.2μm
10.8μm
8.8μm
3000.
2000.
1000.
Wavenumber (cm-1)
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)